

Screening Study of Different Amine-Based Solutions as Sorbents for Direct CO₂ Capture from Air

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Cite This: *ACS Sustainable Chem. Eng.* 2020, 8, 14013–14021

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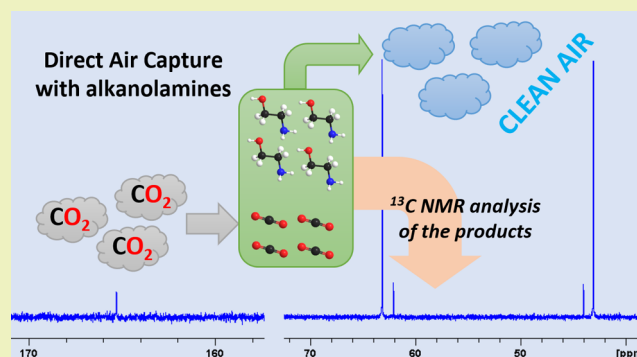
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ABSTRACT: Direct air capture (DAC) is an emerging technology that can help limit the global temperature rises, as it has the potential to contrast the dispersed CO₂ emissions coming from transport and heating that cannot be captured with traditional CCS methods. Although recent improvements are bringing DAC closer to commercial feasibility, an obstacle to its diffusion is the high regeneration energy required by the most common liquid sorbents, Na or K hydroxides. To develop efficient and more sustainable sorbents, in this screening study, several alkanolamines, particularly those already known for their utilization in CCS, were tested for DAC. The percentage of CO₂ absorbed from compressed air of their 1.5 mol dm⁻³ aqueous solutions was evaluated in 24 h capture experiments, and the species formed were identified and quantified by means of ¹³C NMR spectroscopy. For selected amines, their performance in organic diluents was also evaluated. The correlations between aerial CO₂ absorption, chemical structures of the different amines, and species formed in solution have shown that a high yield production of amine carbamate is the decisive factor for an effective CO₂ capture and that aqueous primary unhindered amines are as efficient as aqueous alkali hydroxides, with the potential of a lower regeneration energy.

KEYWORDS: carbon dioxide capture, direct air capture, DAC, alkanolamine, ¹³C NMR speciation, amine carbamates



INTRODUCTION

The recent climate conference COP21 (Paris, 2015) underlined the need to take actions by most of the world's countries to mitigate climate change and keep the global temperature rise well below 2 °C above preindustrial levels.¹ In addition to the reduction of the combustion of fossil fuels and the improvement of the CO₂ capture from large-point sources, the so-called carbon capture and sequestration (CCS) technology,^{2,3} a strategy that is emerging as crucial for achieving the ambitious Paris' target, is the development of negative emission technologies (NETs).⁴ NETs relate to CO₂ removal from the atmosphere through techniques such as the chemical CO₂ capture from ambient air, called direct air capture (DAC).⁵ DAC is a developing technology with the potential to contrast the dispersed emissions coming from transport and residential heating, which cannot be captured at their sparse sources and represent approximately half of the annual anthropogenic CO₂ emissions.^{6,7} In the DAC process, large air-absorbent contactors equipped with many fans blow the air to the absorber, where the ultradiluted CO₂ (approximately 410 ppm) is selectively removed and the "clean" air is returned to the atmosphere. Afterward, the sorbent is regenerated and the captured CO₂ is released for disposal or, more interestingly, for direct utilization, as, for example, in the catalytic methanation.⁸ Moreover, DAC systems benefit from

their inherent flexibility of placement, and careful location planning can favor the use of renewable energy and can reduce the cost of CO₂ transportation from the capture site to the storage or utilization sites.⁹ An ideal DAC process should combine a quick and efficient CO₂ capture with low-energy inputs for air handling, sorbent regeneration, and CO₂ release. Although DAC processes were considered prohibitively expensive until a few years ago, with costs in the range 200–1000 \$/ton of CO₂ (10 times higher than conventional capture from flue gas), the most recent economic analyses suggest that with the latest improvements (mainly engineering) the DAC technology is approaching commercial viability, with capturing costs that can be reduced to less than 100 \$/ton of CO₂.^{10–12} In particular, several studies demonstrated that an air–liquid cross-flow scheme, which reduces the pressure drop, can dramatically lower the capture cost.⁹

So far, the main potential technologies involve chemisorbent materials;⁶ in particular, many researchers have focused on the

Received: May 21, 2020

Revised: August 18, 2020

Published: August 28, 2020



Table 1. Name, Acronym, and Chemical Structure of the Selected Amines and Organic Diluents

	Name	Acronym	Chemical structure	CAS number
Primary	2-aminoethanol	MEA		141-43-5
	2-(2-aminoethoxy)ethanol	DGA		929-06-6
	1-amino-2-propanol	1A2P		78-96-6
	2-amino-1-butanol	2A1B		96-20-8
	2-amino-2-methyl-1-propanol	AMP		124-68-5
	2-amino-2-methyl-1-3-propanediol	AMPD		115-69-5
	2-amino-2-(hydroxymethyl)-1,3-propanediol	TRIZMA		77-86-1
Secondary	2-(methylamino)ethanol	MMEA		109-83-1
	2-(ethylamino)ethanol	EMEA		110-73-6
	2-(butylamino)ethanol	BUMEA		111-75-1
	2-(tertbutylamino)ethanol	TBMEA		4620-70-6
	Diethanolamine	DEA		111-42-2
	bis(2-hydroxypropyl)amine	DIPA		110-97-4
Tertiary	2-(dimethylamino)ethanol	DMMEA		108-01-0
	N methyl diethanolamine	MDEA		105-59-9
Diluents	ethylene glycol	EG		107-21-1
	1-propanol	PrOH		67-63-0
	diethylene glycol monoethyl ether	DEGMEE		111-90-0

development of solid-based sorbent systems, especially immobilized amine/silica sorbents or hollow fiber sorbents.^{13–18} Alkaline liquid sorbents have also been taken into consideration for their fast and efficient CO₂ capture in continuous (not batch) processes;⁶ however, their development has so far been limited due to the high costs of regeneration. Aqueous solutions of sodium and potassium hydroxide have been extensively studied as sorbents for DAC processes for their strong alkalinity and their high reaction rate even with ultradiluted CO₂.^{19,20} Despite a good capture efficiency, the process is energy intensive: the sorbent regeneration is based on the formation of CaCO₃ by adding Ca(OH)₂, and the subsequent calcination of CaCO₃ to release pure CO₂ requires very high temperatures (900 °C), which entail high energy costs, up to 180 kJ/mol CO₂.^{9,10,19}

With the aim of developing new liquid sorbents for the efficient capture of ultradiluted aerial CO₂ with a lower regeneration energy compared to KOH and NaOH solutions, we decided to investigate the performance of several amine-based sorbents in DAC systems. Aqueous amines are well-known (and widely investigated) sorbents for the efficient CO₂ capture from large-scale emission points (CO₂ 12–15% v/v), which can be regenerated at $T = 100–120$ °C, a temperature well below that required for the CaCO₃ calcination.^{21,22}

Currently, many researchers are working to develop innovative amine-based absorbents able to combine the most efficient CO₂ capture with the lowest heat of CO₂ desorption,^{23–26} an important parameter for assessing the regeneration energy (the opposite of the heat of CO₂ absorption, usually lower than 90 kJ/mol CO₂ for all of the most studied aqueous amines).^{22,27}

In this screening study, different types of amines have been compared as DAC sorbents under the same operating conditions to identify the chemical peculiarities crucial for a more efficient CO₂ capture from air: several aqueous alkanolamine solutions have been tested in absorption experiments lasting 24 h, and the measured percentages of CO₂ absorbed have been correlated with the chemical properties of the different amines. The carbonated species formed upon the CO₂ uptake and their relative amounts were evaluated by ¹³C NMR spectroscopy, a powerful noninvasive analytical technique that can provide valuable information on the absorption mechanism.^{28,29} The performances of some amines have also been investigated in organic diluents, namely, in diethylene glycol monoethyl ether (DEGMEE) or in a 1:1 (volume scale) mixture of ethylene glycol (EG) and 1-propanol (PrOH). The higher solubility of CO₂ in organic diluents than in water, and the lower heat capacity and vapor pressure of organic diluents compared to water, could enhance

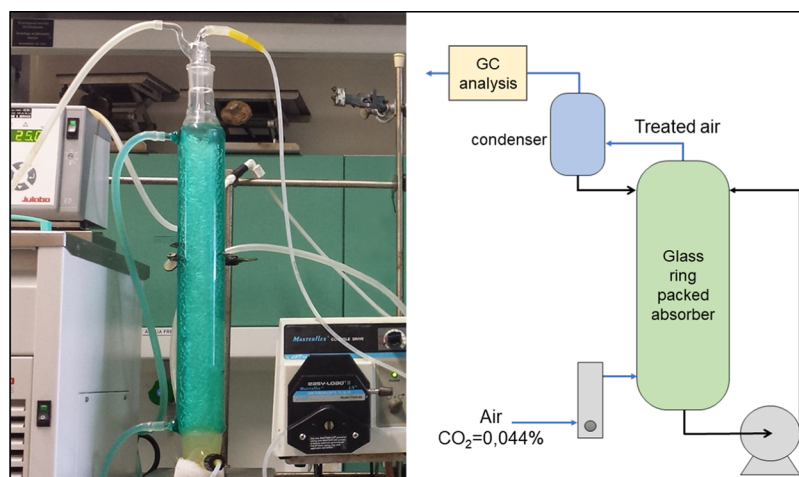


Figure 1. Apparatus for the determination of the percentage of CO₂ absorbed and its schematic flow diagram. Blue lines refer to air and black lines to the liquid sorbent.

the CO₂ absorption and reduce the heat required for the sorbent regeneration: as a matter of fact, several studies have shown that the use of organic diluents instead of water can lower the desorption temperature well below 100 °C.^{30–33} Moreover, we have recently verified that, for the same amine, the heat of CO₂ desorption in organic solutions is lower than in aqueous solution.³⁴

The CO₂ capture performances of the different alkanolamine solutions were compared, in the same operating conditions, with those of aqueous NaOH, sodium carbonate, and potassium glycinate, some of the most commonly proposed sorbents in DAC processes. Moreover, some similarities with general performance trends for amine-based solid sorbents have been highlighted.

MATERIALS AND METHODS

General Information. All of the organic diluents and the amines (Sigma-Aldrich) were reagent grade and were used as received without further purification. A gas controller (Cole Parmer) was used to measure the flow rate of the compressed air. The concentration of aerial CO₂ entering and exiting the absorption column was determined with a Varian CP-4900 gas chromatograph.

The CO₂ percentage measured in the compressed air used was 0.044%. Due to the low amount of CO₂ in air, the amine concentration was fixed at 1.5 mol dm^{−3} for all of the tested solutions (usually, in the CCS process, the amine concentration is in the range 3–5 mol dm^{−3}). In this study, we have considered a large variety of amines such as primary, secondary, tertiary, and sterically hindered amines: their names, chemical structures, and CAS numbers are reported in Table 1, together with those of the used organic diluents.

Experiments of CO₂ Absorption from Air. The percentage of CO₂ absorbed from air by the different amine solutions was evaluated in a home-built glass cylinder with the internal diameter of 56 mm and the height of 400 mm, equipped with an external jacket (Figure 1). The absorber temperature was kept at 25 °C by circulating a thermostatted liquid (by means of a Julabo model F33-MC bath) through the jacket of the column. The gas–liquid contactor column was packed with glass rings with a diameter of 5 mm and charged with 0.100 dm³ of the sorbent. The packing maximizes the exchange surface between air and the sorbent and provides the reaction mixture with a sufficient residence time. The apparatus was designed to operate in a counter current mode: the compressed air (CO₂ 0.044% v/v) was continuously introduced from the bottom of the column, at a flow rate of 46.5 dm³ h^{−1} (8.36 × 10^{−4} mol CO₂ h^{−1}), while the liquid sorbent was introduced from the top of the column; a peristaltic pump (Masterflex) allows the sorbent to circulate continuously from

the bottom to the top of the column at the desired flow rate (0.3 dm³ h^{−1}). The apparatus used and its simplified sketch are reported in Figure 1. The CO₂-depleted air, exiting from the top of the absorber, was dried by flowing in turn through a condenser cooled at −5 °C, a concentrated H₂SO₄ solution, and a gas purification tower filled with P₂O₅, to remove all of the possible amine, solvent, and water traces before being analyzed by the gas chromatograph. The comparison between the amount of CO₂ in inlet and outlet air allowed us to continuously evaluate the percentage of CO₂ absorbed (abs %). All of the experiments were stopped after 24 h.

¹³C NMR Spectroscopy. ¹³C NMR spectroscopy allows the identification of the carbonated species formed in solution after the CO₂ uptake and the evaluation of their relative amounts.^{35–39} Here, after each absorption experiment, a sample of the solution was analyzed with a Bruker Avance III 400 spectrometer operating at 100.613 MHz using a procedure that has already been described in previous studies.^{40,41} Details of the experimental settings and procedures are reported in the Supporting Information, together with two examples of ¹³C NMR spectra before and after the CO₂ absorption (Figures S1 and S2). The percentage of carbamate formed with respect to the total amine (% Am tot) was calculated as the ratio between the area of the carbamate peak and the sum of the areas of the carbamate peak and of the peak of the rapidly equilibrating (free amine)/(protonated amine). All of the reported spectra refer to 24 h of absorption. The spectra relating to 1 h of absorption were not reported because the signals of the carbonated species had too low intensity to be identified.

RESULTS AND DISCUSSION

Aqueous Systems. The reaction of CO₂ with aqueous amine solutions entails several equilibria,^{21,22,29,39} shown by eqs 1–7, taking a primary amine (R₁NH₂) as an example

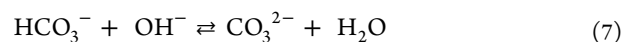
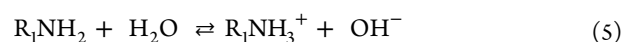
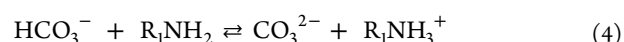
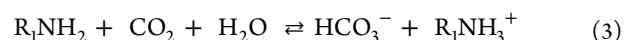
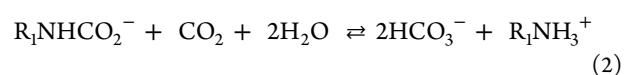


Table 2. Percentage of CO₂ Absorbed (abs%) after 1 and 24 h and Average Values, the Total Amount (mol) of Absorbed CO₂ in 24 h, Absolute (mol) and Relative Amounts of Carbamate Formed (% with Respect to the Total Amount of Amine, % Am tot), and the Percentage of CO₂ Captured as Carbamate^a

entry	amine (or basic species)	pK _b at 25 °C	abs%			CO ₂ abs 24 h (mol)	carbamate		
			at 1 h (%)	at 24 h (%)	average (%)		mol	% Am tot	% CO ₂ abs as carbamate
1	NaOH	/	86.4	88.3	88.1	0.0177	/	/	/
2	Na ₂ CO ₃	/	20.4	11.8	16.9	0.0034	/	/	/
3	K ⁺ Gly ⁻	/	89.3	89.3	89.6	0.0180	0.0175	11.7	97.2
4	MEA	4.49 ⁴²	86.9	87.4	87.3	0.0175	0.0164	10.9	93.7
5	DGA	4.38 ⁴³	85.8	84.8	85.5	0.0172	0.0150	10.0	87.2
6	1A2P	4.50 ⁴²	88.8	87.9	88.4	0.0177	0.0177	11.8	100
7	2A1B	4.40 ⁴³	87.7	85.0	87.1	0.0175	0.0167	11.1	95.4
8	AMP	4.29 ⁴²	76.9	65.4	72.3	0.0145	/	/	/
9	AMPD	5.16 ⁴²	45.7	22.1	32.5	0.0065	/	/	/
10	TRIZMA	5.78 ⁴³	34.7	10.6	22.2	0.0045	/	/	/
11	MMEA	4.12 ⁴²	88.4	89.1	88.9	0.0178	0.0143	9.5	80.3
12	EMEA	4.00 ⁴²	86.1	85.1	85.9	0.0172	0.0097	6.5	56.4
13	BUMEA	4.28 ⁴³	85.9	83.5	85.2	0.0171	0.0114	7.6	66.7
14	TBMEA	3.96 ⁴⁴	64.8	48.8	56.3	0.0113	/	/	/
15	DEA	5.12 ⁴²	78.4	70.2	74.5	0.0150	0.0122	8.1	81.3
16	DIPA	5.12 ⁴²	65.7	50.1	57.8	0.0116	0.0111	7.4	95.7
17	DMMEA	4.43 ⁴²	48.3	36.6	40.8	0.0082	/	/	/
18	MDEA	5.43 ⁴⁵	41.8	14.2	26.6	0.0053	/	/	/

^a"/" indicates that the carbamate is not formed. pK_b of the different amines is also reported.

where R₁NHCO₂⁻ denotes the carbamate of the amine.

The same equations occur with aqueous secondary amines (R₁R₂NH). Equations 1 and 2 do not apply to tertiary amines (R₁R₂R₃N) that are unable to form carbamates due to the lack of hydrogen atoms on the amine functionality.^{29,39}

The percentage of CO₂ absorbed (abs%), defined as the ratio between the amount of captured CO₂ and the CO₂ in the air stream, is a useful parameter for evaluating and comparing the absorbent efficiency of the different amine solutions in a DAC system. The determination of the CO₂ captured from air was carried out with the apparatus depicted in Figure 1, charged with 0.100 dm³ of the 1.5 mol dm⁻³ amine solution, at constant T = 25 °C. Abs% was continuously monitored during the whole 24 h experiment by measuring the CO₂ concentration in the air exiting from the top of the column with a gas chromatograph. At the end of the absorption experiment, the species present in solution were identified and quantified by means of ¹³C NMR analysis.

In Table 2 are reported all of the experimental results obtained with the aqueous solutions tested. The average abs% for the 24 h of the experiment has been reported together with the actual percentages of CO₂ absorbed measured after 1 h and at the end of the experiment (24 h), to evaluate the variation of the capture efficiency over time. For an easier comparison, the actual values of abs% have also been reported in Figure S3 in the Supporting Information. The amount of carbamate formed in solution (mol) and its relative percentage with respect to the total amine in solution (indicated as "% Am tot") have been determined by ¹³C NMR analysis, as previously described. The percentage of the CO₂ captured as carbamate (mol carbamate/mol CO₂ absorbed) has also been reported. The total CO₂ absorbed (mol) in 24 h can be calculated from the average value of abs% and the CO₂ flow rate (8.36 × 10⁻⁴ mol CO₂ h⁻¹). The amount of bicarbonate/carbonate formed has not been directly determined by ¹³C NMR analysis because the corresponding signal was too weak to provide an accurate

quantitative result, and its value can be deduced from the difference between the total absorbed CO₂ (mol) and the carbamate (mol) found in solution.

For comparative purposes, the performances of some commonly proposed sorbents for DAC processes, aqueous solutions of NaOH, sodium carbonate, and potassium glycinate, were tested in the same apparatus with the same operating condition, and the results are reported in Table 2 (entries 1–3).

As a first general result, the highest values of average abs% were obtained with aqueous solutions of unhindered primary and secondary amines. In particular, the high efficiency of aqueous solutions of MEA, DGA, 1A2P, 2A1B, MMEA, EMEA, and BUMEA was not substantially different from that of aqueous solutions of NaOH and glycinate, and those values were maintained almost unchanged for the whole experiment. The secondary amines DEA and DIPA and the tertiary amines MDEA and DMMEA, as well as the sterically hindered amines AMP, AMPD, TRIZMA, and TBMEA, were the less efficient absorbents. It is noteworthy that these performance trends are almost the same as those found for amine-based solid adsorbents: many studies show that the best adsorption is obtained with immobilized primary amines, while tertiary and sterically hindered amines perform poorly.^{46–48} However, the aforementioned general results deserve more in-depth considerations, to correlate the efficiencies with the chemical structures of the amines used.

As a general finding, in the aqueous sorbents with the highest abs% (MEA, DGA, 1A2P, 2A1B, and MMEA), most of CO₂ is captured as carbamate (eq 1). In particular, the amount of carbamate formed corresponds almost entirely (between 80 and 100%) to the amount of CO₂ captured in the 24 h of absorption. After 24 h, with an air flow of 46.5 dm³ h⁻¹, approximately 0.02 moles of CO₂ should be passed through the column: consequently, the maximum amount of carbamate that can be produced with a 100% absorption is 0.02 moles (eq

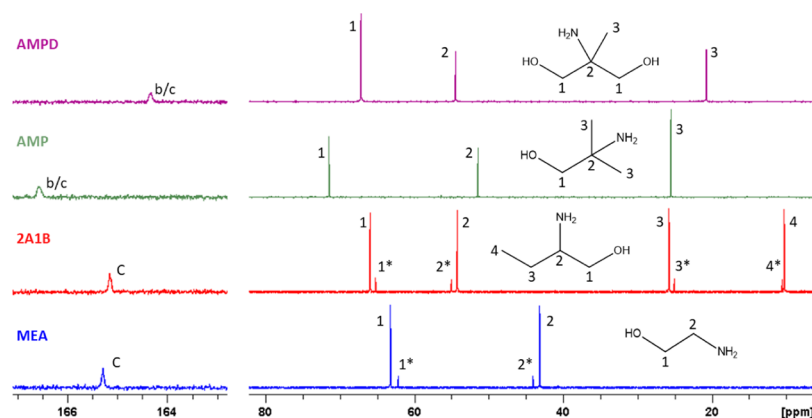
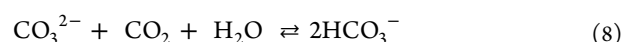


Figure 2. ^{13}C NMR spectra of aqueous MEA, 2A1B, AMP, and AMPD at the end of the absorption experiment. The numbers indicate the carbon atoms referred to both free and protonated amine fast exchanging in the NMR scale. Asterisks denote the chemical shifts of carbon backbones of amine carbamate. C indicates the carbonyl atoms of amine carbamate, while b/c refers to the signal of fast exchanging bicarbonate/carbonate ions. The intensity of the signals at 163–167 ppm is not in scale.

1), corresponding to approximately 13.3% of the starting amine (0.15 mol) in the sorbent: at the end of the absorption process, the amount of the amines is always much greater than the absorbed CO_2 .

The residual captured CO_2 , which has not been converted into carbamate (20%, at most), is present in solution as bicarbonate/carbonate (eqs 3, 4, and 6). DMMEA and MDEA are tertiary amines and cannot form carbamate, while AMP, AMPD, TRIZMA, and TBMEA are sterically hindered amines and their carbamates are very unstable: the CO_2 absorption in their aqueous solutions produces only bicarbonate/carbonate ions.⁴⁹ Although the bicarbonate formation (overall amine/ CO_2 stoichiometry of 1:1) improves the CO_2 solubilization into the amine solution compared to the formation of carbamate (eq 1, overall amine/ CO_2 stoichiometry of 2:1),^{36,39} those amines are the least efficient, and quite interestingly, their efficiency strongly decreases with time. Moreover, the abs% order TBMEA > DMMEA > AMPD > MDEA > TRIZMA corresponds to the decrease of the alkalinity (pK_b values from Table 2: 3.96, 4.43, 5.16, 5.43, and 5.78, respectively).

Very likely, the reaction rate between the sorbent and CO_2 is the most incisive parameter for the efficiency of the capture of CO_2 from the air. We have found in our previous studies on liquid amines^{34,50} that the formation of the carbamate derivatives is more kinetically favored than the bicarbonate/carbonate species, and the same has been found by other researchers during studies on amine-based solid adsorbents for DAC processes.^{16,47} The great excess of unhindered primary and secondary amines in solution compared to the low amount of CO_2 in air favors the rapid formation of carbamate (stoichiometry 2:1) rather than bicarbonate (stoichiometry 1:1). Those amines show a much higher reaction rate and consequently greater abs% than the sterically hindered and tertiary amines (Figure S4, Supporting Information). The marked decrease of the abs% over time of these latter amines could be due to the decrease of the OH^- concentration (eq 5) with the increasing protonated amine (R_1NH_3^+) concentration, which decreases the formation of bicarbonate/carbonate. A further confirmation of the importance of the reaction rate comes from the very low percentage of CO_2 absorbed found for the sodium carbonate solution (Table 2, entry 2), in spite of the favorable equilibrium of the reaction



It is well known that the main drawback of the carbonate sorbent for CCS processes is due to the low reaction rate, compared to conventional amine- or ammonia-based systems,⁵¹ and the same occurs for DAC processes (Figure S4).

In Figure 2 are reported the ^{13}C NMR spectra of some aqueous primary amines (MEA, 2A1B, AMP and AMPD) at the end of the 24 h absorption. The relative amount of MEA and 2A1B carbamate (carbonyl signal at approximately 165 ppm) can be computed from the accurate integration of the peak signal of each $-\text{CH}_2-$ resonance, in the range 10–80 ppm. On the contrary, AMP and AMPD cannot form carbamate and the signal in the range 163–167 should be ascribed to bicarbonate/carbonate ions.

By considering MEA (Table 2, entry 4) as the absorption reference for aqueous primary amines, it is possible to evaluate the influence of groups attached to the carbon adjacent to the amino function (α -carbon) on the percentage of CO_2 absorbed. The abs% and the amount of carbamate formed in aqueous DGA, 1A2P, and 2A1B (Table 2, entries 5, 6, and 7 respectively) suggest that a single or two alkyl groups attached to the α -carbon do not have significant effects on the CO_2 absorption mechanism for carbamate formation and, consequently, for the high CO_2 absorption.

Instead, the steric hindrance due to the three alkyl groups attached to the α -carbon in AMP, AMPD, and TRIZMA (Table 2, entries 8, 9, and 10, respectively) prevents the formation of the carbamate, and the CO_2 absorption occurs only through the formation of bicarbonate and, to a least extent, carbonate ions (reactions 3, 4, and 6), with a lower reaction rate and abs%. The worse absorption performances of AMPD and TRIZMA, compared to AMP, are presumably related to the number of $-\text{OH}$ (electron attractors) attached to the α -carbon that reduces the electron density of the nitrogen of the amino group, thus affecting the mechanism of the CO_2 reaction. As a matter of fact, their abs% decreases with decreasing alkalinity. It is worth noting that aqueous AMP is among the most efficient sorbents in the conventional CCS process: its poor performance in the DAC process underlines the importance of the kinetic parameter in the CO_2 capture from air.

As previously stated, in the most efficient amines (primary amines MEA, DGA, 1A2P, 2A1B, secondary amine MMEA,

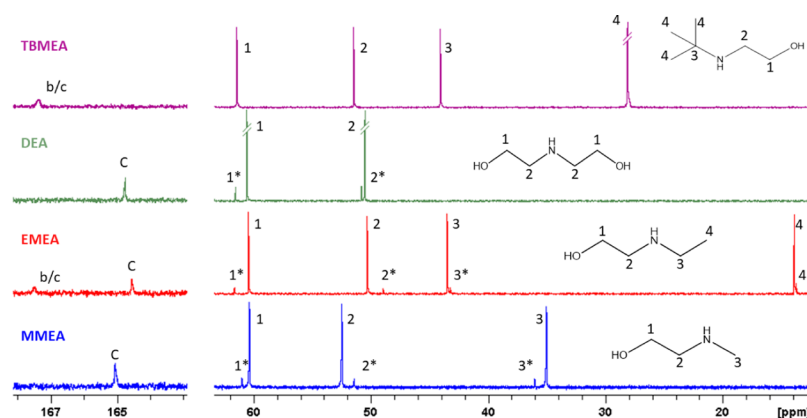


Figure 3. ^{13}C NMR spectra of aqueous MMEA, EMEA, DEA, and TBMEA at the end of the absorption experiment. The numbers indicate the carbon atoms referred to both free and protonated amine fast exchanging in the NMR scale. Asterisks denote the chemical shifts of carbon backbones of amine carbamate. C indicates the carbonyl atoms of amine carbamate, while b/c refers to the signal of fast exchanging bicarbonate/carbonate ions. The intensity of the signals at 163–168 ppm is not in scale.

Table 3. Percentage of CO_2 Absorbed (abs%) of the Different Absorbents Measured after 1 and 24 h and Average Values, the Total Amount (mol) of Absorbed CO_2 in 24 h, Absolute (mol) and Relative Amounts of Carbamate Formed (% with Respect to the Total Amount of Amine, % Am tot), and the Percentage of CO_2 Captured as Carbamate^a

entry	amine	diluent	abs%			CO_2 abs 24 h (mol)	carbamate		
			at 1 h (%)	at 24 h (%)	average (%)		mol	% Am tot	% CO_2 abs as carbamate
1	MEA	H_2O	86.9	87.4	87.3	0.0175	0.0164	10.9	93.7
2		EG/PrOH	85.6	82.4	84.7	0.0170	0.0138	9.2	81.2
3		DEGMEE	89.3	44.9	67.0	0.0134	0.0108	7.2	80.6
4	DGA	H_2O	85.8	84.8	85.5	0.0172	0.0150	10.0	87.2
5		EG/PrOH	87.9	76.1	83.1	0.0167	0.0132	8.8	79.0
6		DEGMEE	85.2	32.7	57.4	0.0115	0.0111	7.4	96.3
7	AMP	H_2O	76.9	65.4	72.3	0.0145	/	/	/
8		EG/PrOH	52.2	7.6	29.7	0.0060	/	/	/
9		DEGMEE	13.0	7.4	9.8	0.0020	/	/	/
10	EMEA	H_2O	86.1	85.1	85.9	0.0172	0.0097	6.5	56.4
11		EG/PrOH	82.4	32.8	57.7	0.0116	0.0063	4.2	54.3
12		DEGMEE	71.3	3.1	28.4	0.0057	0.0030	2.0	52.6
13	BUMEA	H_2O	85.9	83.5	85.2	0.0171	0.0114	7.6	66.7
14		EG/PrOH	79.3	23.7	51.6	0.0104	0.0065	4.3	62.5
15		DEGMEE	65.4	4.8	26.8	0.0054	n.d.	n.d.	/

^a“n.d.” relates to a very low amount of carbamate, not detectable with the ^{13}C NMR technique, while “/” indicates that the carbamate is not formed.

Table 2), most of CO_2 is converted into carbamate. However, the features of the secondary amines EMEA, BUMEA, DEA, and DIPA deserve an explanation because the percentage of carbamate is not a measure of the percentage of CO_2 absorbed. The ^{13}C NMR spectra of some aqueous secondary amines at the end of the experiment are reported in Figure 3.

MMEA (Table 2, entry 11) displays both the higher absorption and the greater amount of carbamate formed: as shown in the spectral range 163–168 ppm, aqueous MMEA reacts with aerial CO_2 , producing only carbamate. On the other hand, aqueous EMEA and BUMEA (Table 2, entries 12 and 13) have high abs% (85.9 and 85.2%, respectively) but a relatively low carbamate percentage (56.4 and 66.7%, respectively). The high alkalinity of EMEA and BUMEA can contribute to their high efficiency, due to the formation of an appreciable amount of carbonate/bicarbonate (43.6–33.3%, respectively) as evidenced in the EMEA spectrum in Figure 3 (similar spectrum recorded for BUMEA). On the contrary, DEA and DIPA (Table 2, entries 15 and 16) have lower abs% but display a much greater percentage of CO_2 conversion into

carbamate (spectrum of DEA reported in Figure 3, similar spectrum recorded for DIPA). Those results are due to the weaker basicity of the two amines that disfavors the formation of carbonate/bicarbonate, and consequently, most of CO_2 (a low amount, indeed) is captured as carbamate. Finally, TBMEA is the worst absorber among the selected secondary amines (Table 2 entries 14), due to the great steric hindrance of its tert-butyl group, which prevents the formation of carbamate and leads to the formation of only bicarbonate/carbonate, as shown in Figure 3.

Nonaqueous Systems. For some significant amines (MEA, DGA, AMP, EMEA, BUMEA), the percentage of aerial CO_2 absorbed was also investigated in nonaqueous solutions, using DEGMEE or a 1:1 mixture of EG and PrOH as diluents. Recently, we had already studied the advantages of some nonaqueous solutions of the aforementioned amines as CCS sorbents,^{34,50} and it seemed interesting to us to evaluate their capture performance even with ultradiluted CO_2 . The replacement of water with organic diluents has the potential of redirecting the reaction between amines and CO_2 toward

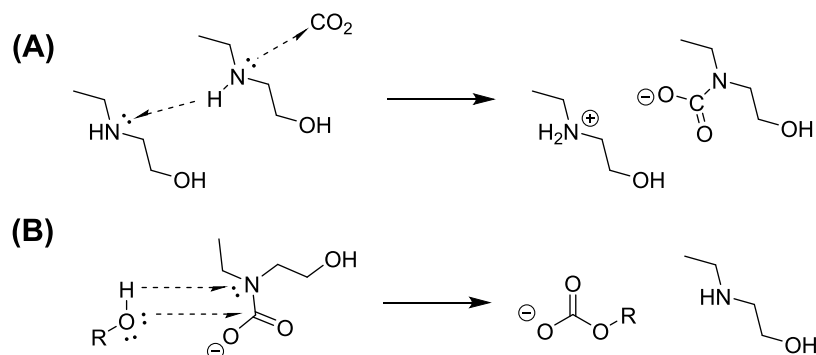
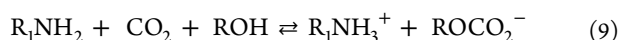


Figure 4. Scheme of the proposed two-step reaction mechanism for the formation of alkyl carbonate in nonaqueous EMEA solutions, including (A) the initial formation of the carbamate of the amine and (B) its subsequent reaction with an alcohol.

less stable carbonated species that require lower temperatures for their regeneration. In the absence of water, the formation of bicarbonate and carbonate ions (reactions 2–7) cannot take place and CO₂ reacts with an excess of both primary and secondary amines to produce the carbamate of the amines (reaction 1). Moreover, organic diluents with hydroxyl groups can react with CO₂ in the presence of a base (in this case, the amine), leading to the formation of alkyl carbonates (in the following equation, R denotes the alkyl groups CH₃CH₂OCH₂CH₂OCH₂CH₂–, HOCH₂CH₂–, or CH₃CH₂CH₂–)^{33,34}



In Table 3 are reported the experimental results obtained for the different solutions tested. For comparison, the result obtained in its aqueous solution is also reported for each amine. The experiments were carried out with the same procedures and operating conditions of the aqueous sorbents. The amount of alkyl carbonate formed at the end of the absorption has not been directly determined by ¹³C NMR analysis because the corresponding signal was too weak to provide an accurate quantitative result: its value can be deduced from the difference between the absorbed CO₂ (mol) and the carbamate (mol) found in solution. For a simpler comparison, the actual values of abs% have also been reported in Figure S5 in the Supporting Information.

The data summarized in Table 3 confirm that, in organic diluents too, the percentage of CO₂ absorbed follows the order of primary amines > secondary amines > AMP.

The primary amines MEA and DGA display similar abs% in aqueous and EG/PrOH solutions. All of the other sorbents are less efficient, in particular in DEGMEE solution, and at the end of the experiments. In DEGMEE, the actual value of abs% at 24 h is more than halved compared to the first hour, whereas aqueous solutions maintain the same high percentage of CO₂ absorbed during the 24 h experiments. The general order of abs% as a function of the diluent is H₂O > EG/PrOH > DEGMEE. This trend is particularly evident for the secondary amines EMEA and BUMEA and for the sterically hindered AMP.

The higher percentage of CO₂ absorbed for all of the amines in EG/PrOH compared with DEGMEE depends on the greater reactivity of CO₂ to form the corresponding alkyl carbonates with EG and PrOH compared to DEGMEE. As already found in previous studies,^{34,50} the longer the alcoholic diluent chain, the lower the stability of alkyl carbonate, and

consequently, the abs% in DEGMEE is lower than in EG/PrOH.

The higher abs% of MEA and DGA in organic diluents with respect to EMEA and BUMEA is due to the greater amount of carbamate (about 80%) formed, compared to alkyl carbonate. As previously reported (Table 2, entries 12 and 13), the formation of bicarbonate substantially contributes (33–44%) to the CO₂ capture in aqueous EMEA and BUMEA, in addition to the formation of carbamate: in the absence of that contribution in nonaqueous diluents, the percentage of CO₂ absorbed of EMEA and BUMEA solutions must decrease. The strong abs% reduction over time of the last two amines seems to indicate that the formation of the alkyl carbonate requires a large excess of the amine. The proposed mechanism for the formation of the alkyl carbonate (taking EMEA as an example) is shown in Figure 4. Initially, EMEA-CO₂[–] (carbamate) and EMEA-H⁺ (protonated) are formed, due to the nucleophilic attack of the amino nitrogen of one EMEA molecule to CO₂ with the consequent deprotonation, promoted by another EMEA molecule (Figure 4A). In the excess of the amine, EMEA carbamate can therefore react with the alcoholic function of the diluent, forming the alkyl carbonate (Figure 4B). The direct reaction between the alcoholic function of the diluent and CO₂ is likewise hampered by a greater activation energy.

Finally, in nonaqueous AMP solutions, neither bicarbonate nor carbamate can be formed, and CO₂ can only be captured as alkyl carbonate (reaction 9): in this case, AMP acts as a base and allows the diluent with an –OH group to react with CO₂.

CONCLUSIONS

With the aim of identifying the most crucial chemical peculiarities for the development of new liquid absorbents for DAC processes, we carried out a screening study on the performance of different aqueous alkanolamine solutions, under the same operating conditions: their ability to absorb CO₂ from an air stream was correlated with their chemical structure and with the species formed by the absorption reaction, and useful information on the reaction mechanism has been obtained. As a general finding, aqueous unhindered primary amines are the most suitable sorbents for DAC processes, as they are as efficient as aqueous alkali hydroxides but with a potential energy saving due to the lower temperatures required for sorbent regeneration. The formation of a high yield of amine carbamate seems to be the decisive factor for an efficient CO₂ capture, but the formation of an appreciable amount of carbonate/bicarbonate because of the

strong basicity of some amines (EMEA, BUEA) can contribute to attain a high percentage of CO₂ absorbed. The amines that are unable to form carbamate have provided poor absorption values. In particular, aqueous AMP, which is a very efficient sorbent in conventional CCS processes, has proven to be poorly suited for the capture of ultradiluted CO₂, due to the lower kinetics of carbonate/bicarbonate formation. These findings highlighted the differences of DAC processes compared to conventional CCS processes and, consequently, the best CCS absorbents cannot be the best choice for the DAC process. The obtained results also showed that aqueous amines are more efficient than the same amines in organic diluents. MEA and DGA in EG/PrOH display slightly lower abs% compared to the aqueous solution by virtue of the high percentage of carbamate formed. In the absence of carbamate formation (as in the case of AMP), CO₂ can only be captured as alkyl carbonate, which is less stable than carbamate and requires a large excess of the free amine as a base. In conclusion, nonaqueous sorbents do not seem suitable for DAC processes, also taking into account that their possible use would entail substantial changes in conventional DAC equipment to limit the solvent loss and consequent environmental issues.

■ ASSOCIATED CONTENT

SI Supporting Information

The Supporting Information is available free of charge at <https://pubs.acs.org/doi/10.1021/acssuschemeng.0c03800>.

¹³C NMR analysis settings and procedures; comparison of ¹³C NMR spectra before and after CO₂ absorption for aqueous MEA and AMP; comparison of the actual abs% (after 1 and 24 h) of all of the tested aqueous and nonaqueous sorbents; comparison of the reaction rate (reported as abs% vs time) for several aqueous absorbents (PDF)

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The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript.

Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

For the financial support, the authors thank the ICCOM Institute of National Research Council, Regione Toscana—POR FSE 2014-2020 as well as the industry partner STM Technologies srl. For the facilities, the Department of Chemistry, University of Florence, is gratefully acknowledged.

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